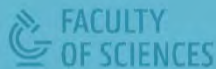


A modelling view on the existence of hysteresis during reactive HiPIMS

K. Strijckmans, D. Depla

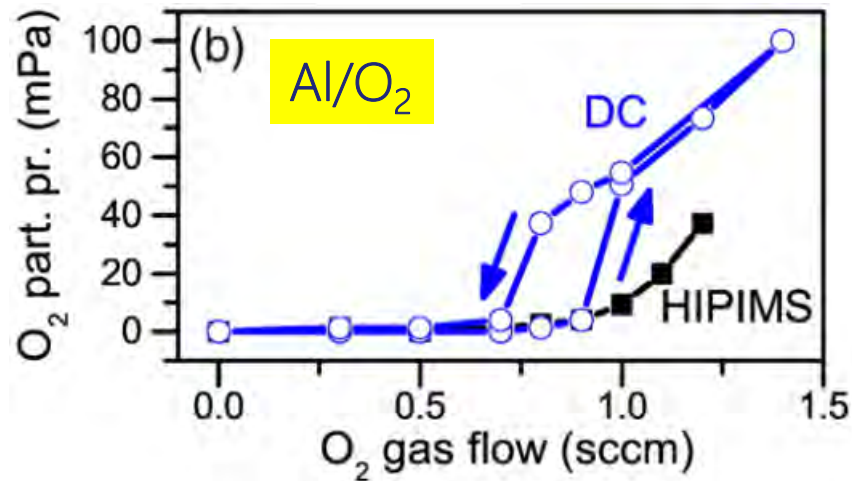
Dedicated Research on Advanced Films, and Targets



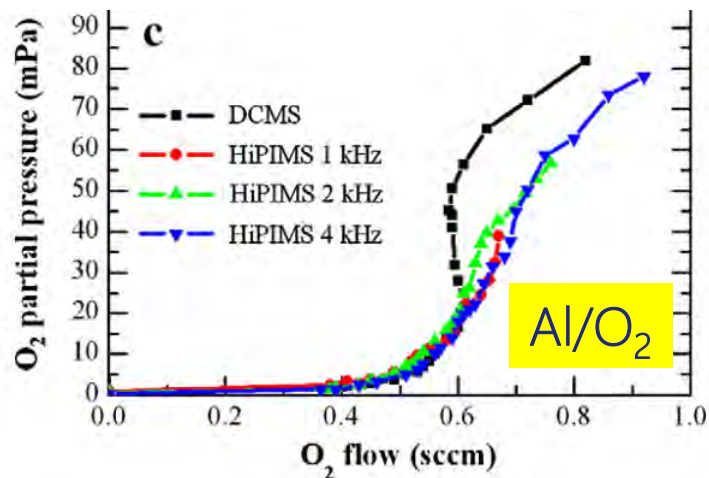
Outline

- 1 Introduction
- 2 RSD models
- 3 Simulation study
- 4 RSD^{+IR} model
- 5 Conclusion

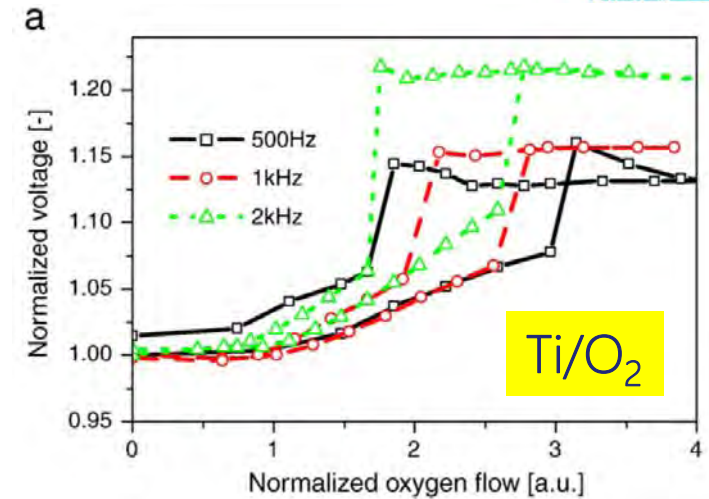
Reactive HiPIMS: hysteresis?



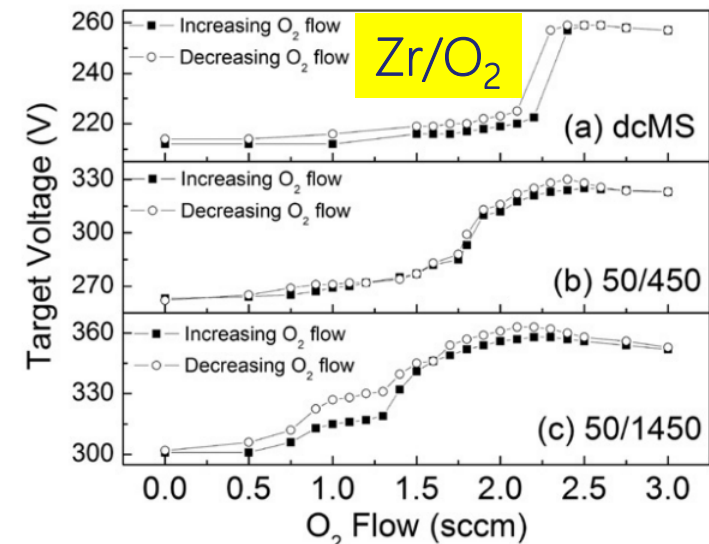
E. Wallin, et al., *Thin Solid Films* 516, 6398 (2008)



M. Aiempanakit, et al., *Thin Solid Films* 519, 7779 (2011)

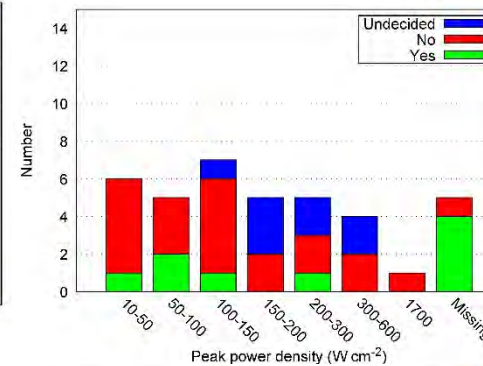
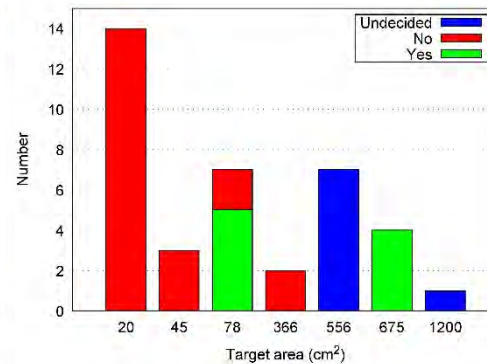
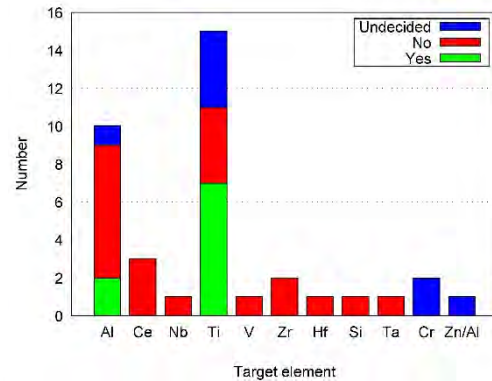


T. Kubart, et al., *Surf. Coat. Tech.* 205, S303 (2011)

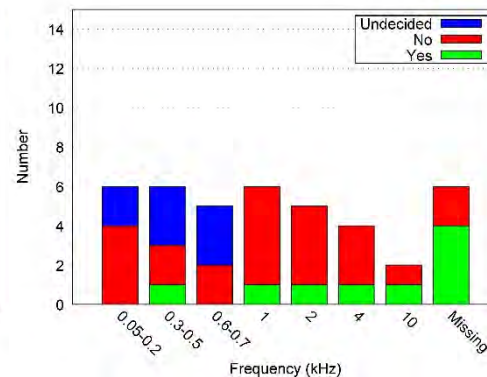
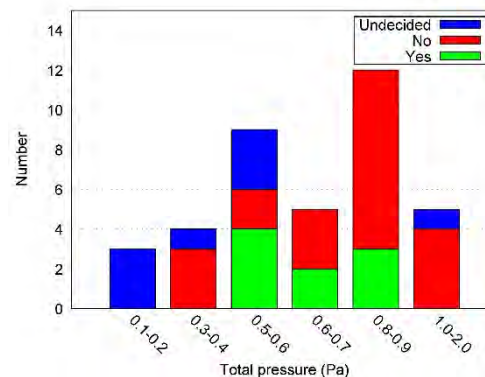
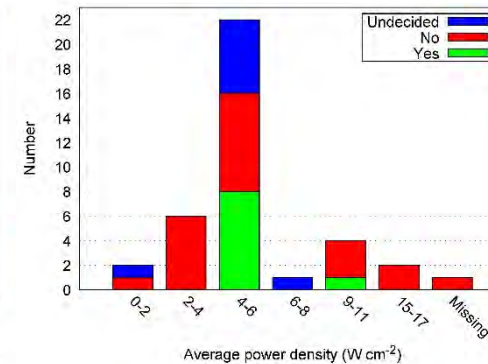
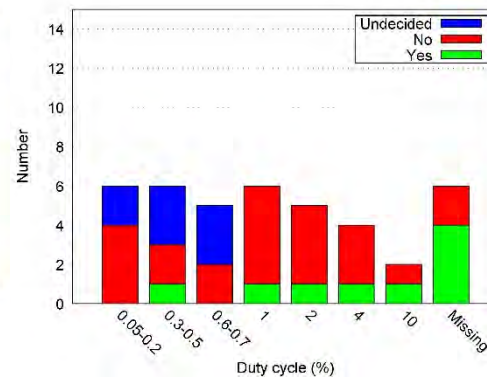
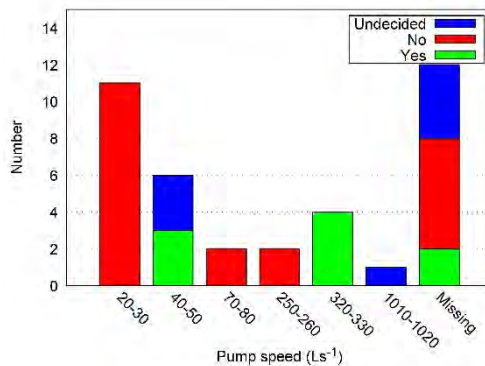


K. Sarakinos, et al., *Surf. Coat. Tech.* 202, 5033 (2008)

Reactive HiPIMS: hysteresis?



Hysteresis?
9 yes
21 no
8 undecided



38 hystereses out of 18 papers

☞ limited data

☞ undecided = fast ramping

⇒ no conclusions

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Variables in RSD model

System part	Resolved variable		Model approach
Chamber	P	reactive partial pressure	one-cell
	Q_p	gas flow to pump	
Target	Q_t	gas flow consumption	one-cell uniform current
• Surface	θ_m	metallic fraction	multi-cell
	θ_c	chemisorbed fraction	non-uniform current
• Subsurface	θ_r	reacted fraction	
	n_m(x)	metal concentration	depth profile
	n_r(x)	reactive gas concentration	SRIM implantation
Substrate	θ_s	chemisorbed fraction	one-cell
	Q_s	gas flow consumption	multi-cell SIMTRA profile

5 **BALANCE** equations \Leftrightarrow 5 **ODE's**

$$0 = f(y) \Leftrightarrow \frac{dy}{dt} = f(y)$$

Steady state \Leftrightarrow **Time**

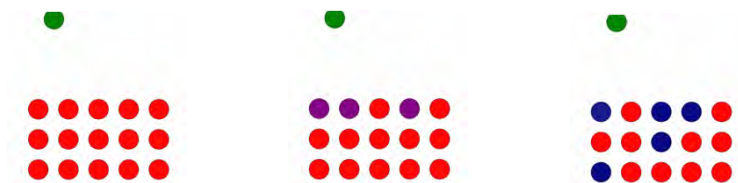
2 **ODE's** \Leftrightarrow 2 **PDE's**

$$0 = f\left(y, \frac{\partial y}{\partial x}\right) \Leftrightarrow \frac{\partial y}{\partial t} = f\left(y, \frac{\partial y}{\partial x}\right)$$

Processes in RSD2013

Target

sputtering



- metal M
- chemisorbed MR
- reacted MR
- reactive molecule R_2
- inert gas Ar
- reactive atom R

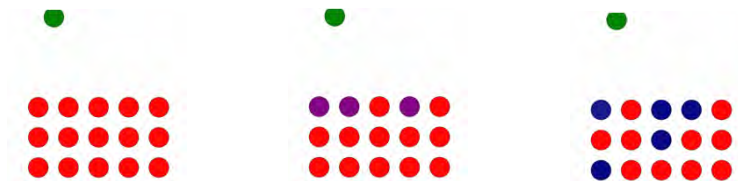
Processes in RSD2013







Target

sputtering



direct implantation

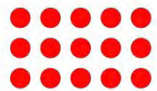


-  metal M
-  chemisorbed MR
-  reacted MR
-  reactive molecule R_2
-  inert gas Ar
-  reactive atom R

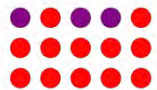
Processes in RSD2013

Target

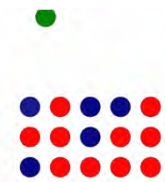
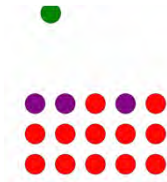
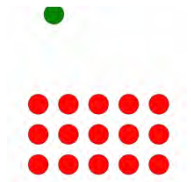
sputtering









direct implantation



knock-on implantation

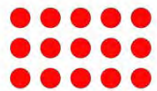


-  metal M
-  chemisorbed MR
-  reacted MR
-  reactive molecule R_2
-  inert gas Ar
-  reactive atom R

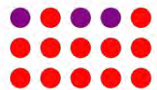
Processes in RSD2013

Target

sputtering

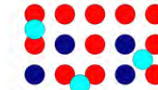








direct implantation



knock-on implantation

reaction

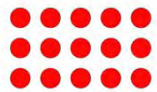


-  metal M
-  chemisorbed MR
-  reacted MR
-  reactive molecule R_2
-  inert gas Ar
-  reactive atom R

Processes in RSD2013

Target

sputtering

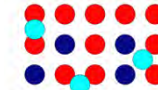


direct implantation



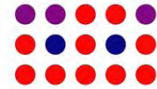
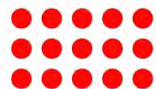
knock-on implantation

reaction



Target & substrate

deposition



metal M



chemisorbed MR



reacted MR



reactive molecule R_2



inert gas Ar

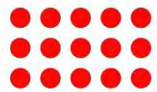
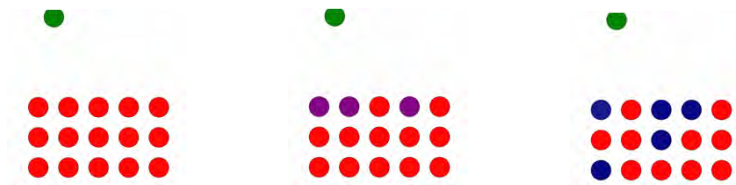


reactive atom R

Processes in RSD2013

Target

sputtering

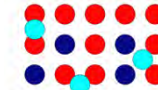


direct implantation



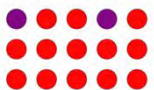
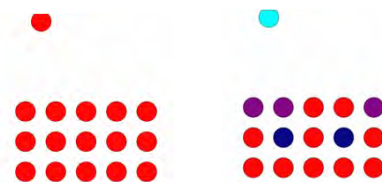
knock-on implantation

reaction



Target & substrate

deposition

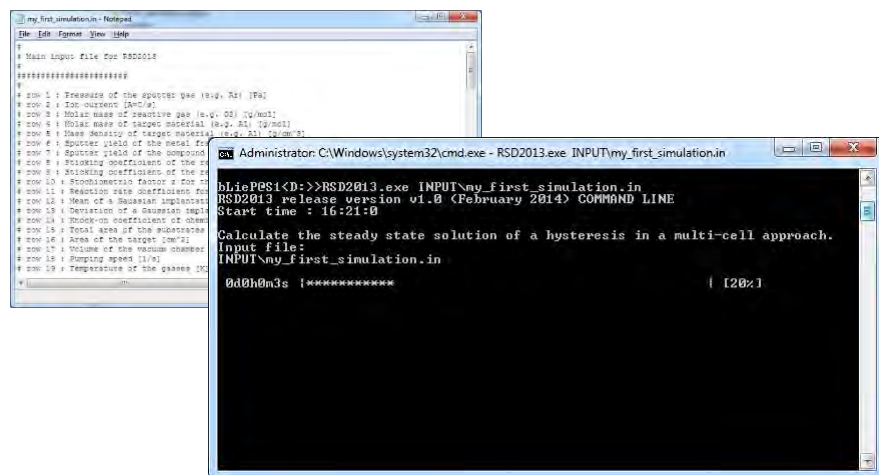


chemisorption

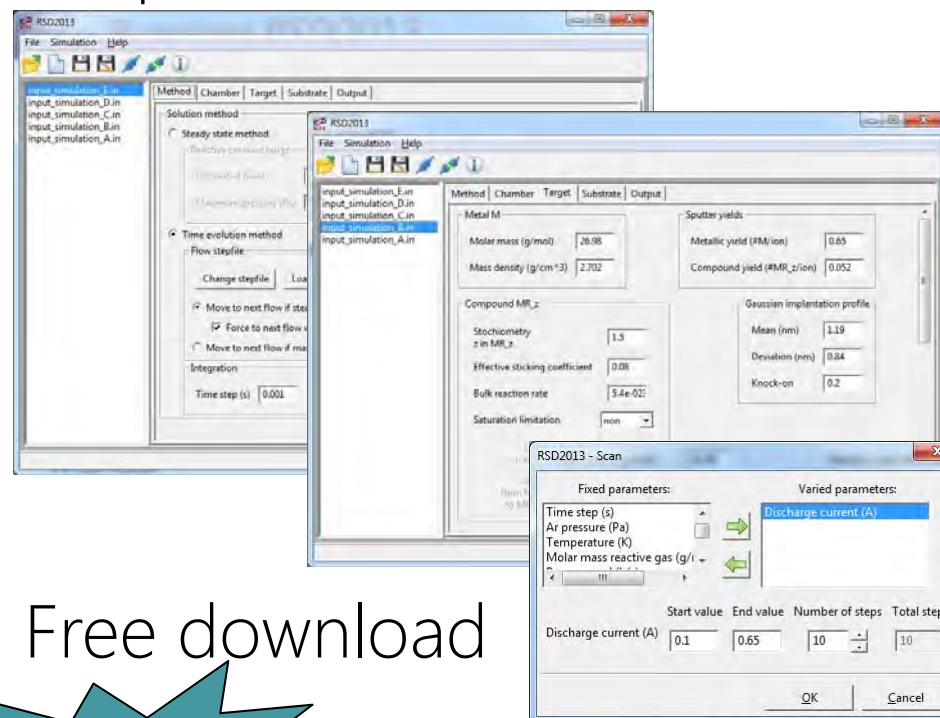
- metal M
- chemisorbed MR
- reacted MR
- reactive molecule R_2
- inert gas Ar
- reactive atom R

Running RSD2013 software

Command line



Graphical user interface (GUI)



Manual

Installation

The RSD2013 software is compiled to run on a Windows platform. It mainly consist out of two executables: `RSD2013.exe` and `RSD2013_gui.exe`. The first executable is the graphical user interface (GUI) which creates the `input_simulation.in` and can start up the RSD2013 simulation. The second executable is the effective simulation program. After generating an input file with the GUI or manually, you can run `RSD2013.exe` on the command line to perform the simulation.

Installation of the RSD2013 software is easy. Simply unzip the compressed zip file to a location of your choice and you are ready to use the software. The directory `data` and `input` should be left intact. Renaming the `RSD2013.exe` executable will make running simulations through the GUI impossible.

Overview

The RSD2013 software is developed to simulate the reactive sputter process of a DC magnetron. Its focus is on the possible hysteresis curve of this process. To this end, it solves the equations of the RSD2013 model, as can be found in following subsections. The nomenclature of the variables used here corresponds with the one of this subsection.

The RSD model calculates following variables:

- the pressure P_0 of the reactive gas in the system
- the compound B_0 , unreacted B_0 and metal B_0 fractions of the target surface
- the compound B_0 and metal fractions of the substrate surface
- the metal concentration n_0 in the target subsurface region
- the compound concentration in the target subsurface region which is directly derived from n_0
- the non reacted implanted reactive gas concentration n_0 in the target subsurface region
- the consumption Q_0 of reactive gas by the target
- the consumption Q_0 of reactive gas by the substrate
- the amount of reactive gas Q_0 pumped away by the vacuum pump
- the amount of reactive gas Q_0 introduced into the vacuum chamber

To the end the RSD model needs several input variables. These input variables are clarified throughout the following sections.

Quick start

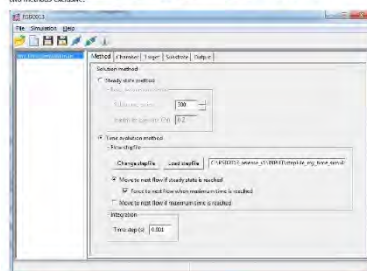
To run a first RSD simulation, you just double click the GUI executable `RSD2013_gui.exe`. By default a complete input is specified in the window tab `input_simulation.in`, `input_simulation.in` and `input_simulation.in`.

All simulation options are visual within the window tabs. None used or relevant options or fields are grayed out and inaccessible. They become (un)accessible depending on which simulation choices you make. For example, when choosing the `Steady state` option in the window tab `Method`, then the fields connected to the `Steady state` option are relevant and as such grayed out.

Most fields have a restricted range of values that can be set. This restriction only applies to the GUI and can be easily corrected by manually editing the `input_simulation.in`.

Method

The window tab `Method` basically specifies how the RSD2013 model should be solved. Its solution method, two options are available: the `Steady state` option and `Time evolution` option. Primarily is the choice between the two methods exclusive.



Method window tabs

Steady state method

To solve the RSD2013 model in its steady state description, the reactive pressure P_0 is stepwise increased up to the `Maximum pressure`, and subsequently decreased. The total number of reactive pressure P_0 values that are calculated are given by the field `Calculated points`.

Calculated points

To define the total number N of reactive pressure P_0 values that are calculated in the `Steady state` method. So the $N/2$ reactive pressure P_0 values are each calculated twice. The first time for an increasing reactive flow Q_0 and the second time for a decreasing reactive flow Q_0 .

Free download

SRIM
www.srim.org

RSD2013 v1
www.DRAFT.ugent.be

SIMTRA v2.2.1-beta
www.DRAFT.ugent.be

Extension of the RSD model to HiPIMS

Model modifications ...

- **RSD^{+P}**
(squared blocked) current pulses
☞ inherent time dependent (only time solution)
- **RSD^{+PR}**
Different oxygen 'activation'
☞ sticking coefficient lowers during pulse off-time
- **RSD^{+PM}**
Metal ionization and implantation
☞ combined ionization-return probability ε_{M+} for sputtered metal atom
☞ metal implantation profile
☞ density relaxation is included



Study the effect on the hysteresis of ...

- Enhanced target cleaning?
- Lower surface reactivity by pulse off-time (and gas rarefaction)
- High dose of metal implantation

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Reference system

Start from a reference DC system of Al in Ar/O₂

Parameters	Value	Description
RSD		
Y_m [#M(R ₂) ion ⁻¹]	0.756	sputter yield of metal atoms M
Y_r, Y_c [#M(R ₂) ion ⁻¹]	0.06	sputter yield of compound molecules MR ₂ , chemisorbed molecules MR ₂
α_t	0.1	sticking probability of reactive gas on metal for target
α_s	0.1	sticking probability of reactive gas on metal for substrate
k [cm ³ s ⁻¹ #M(R ₂) ⁻¹]	5·10 ⁻²³	reaction rate coefficient of implanted reactive atoms with metal particles
β [#R ion ⁻¹]	0.2	knock-on yield of chemisorbed reactive atoms
$p(x)$ [cm ⁻¹]	$R_p=1.4$ nm $dR_p=0.8$ nm	mean of Gaussian implantation profile of reactive atoms deviation of Gaussian implantation profile of reactive atoms
n_0 [#M(R ₂) cm ⁻³]	6.03·10 ²²	particle density
z	1.5	stoichiometric factor
I [A]	0.286	discharge current
P_i [Pa]	0.4	inert working gas pressure
T [K]	300	gas temperature
V [cm ³]	12500	volume of vacuum chamber
A_t [cm ²]	10	area of target
A_s [cm ²]	1000	area of substrate
S [L s ⁻¹]	48.54	gas pumping speed

Low sticking probability

✎ Constant current mode

Average power

- metallic mode ~100 W
- poisoned mode ~70 W

Relative low working pressure

Keep it simple:

- one-cell target
- one-cell substrate

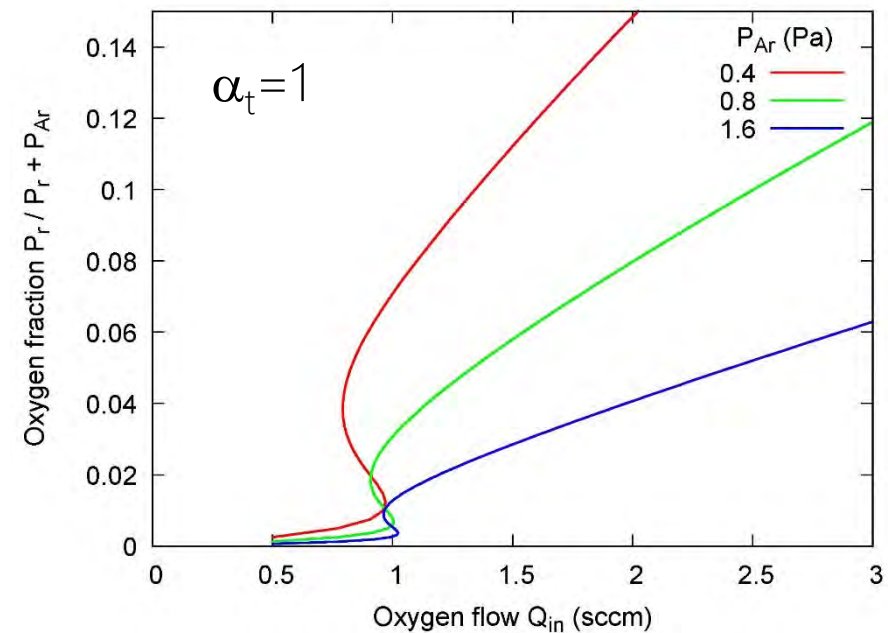
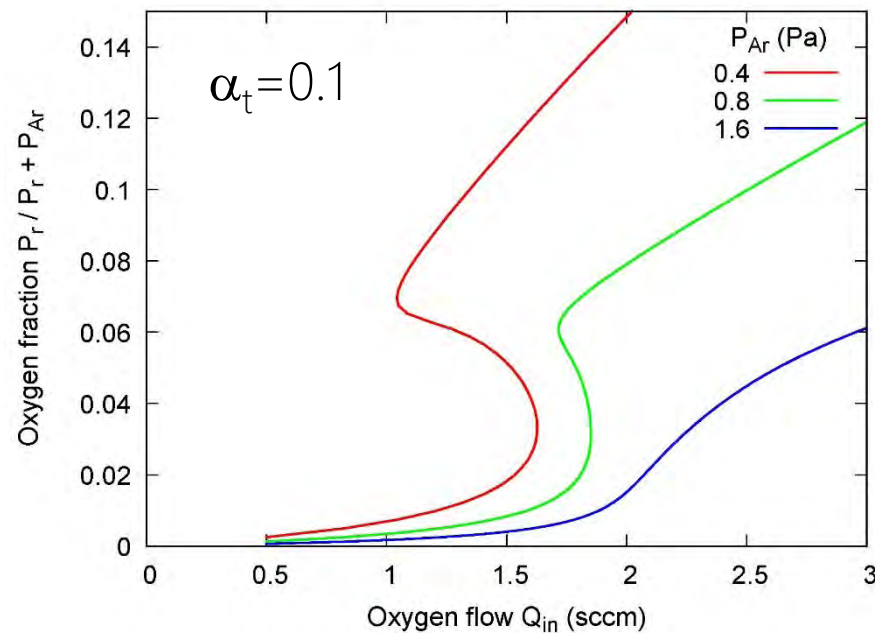
Operation pressure Argon



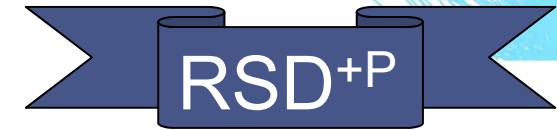
What's the influence of the working pressure in DC ?

- ☞ depends on surface reactivity of gas on target material
- ☞ hysteresis vanishes for low surface reactivity (like Al and Ti) at higher working pressure

⇒ HiPIMS "often" at higher working pressure

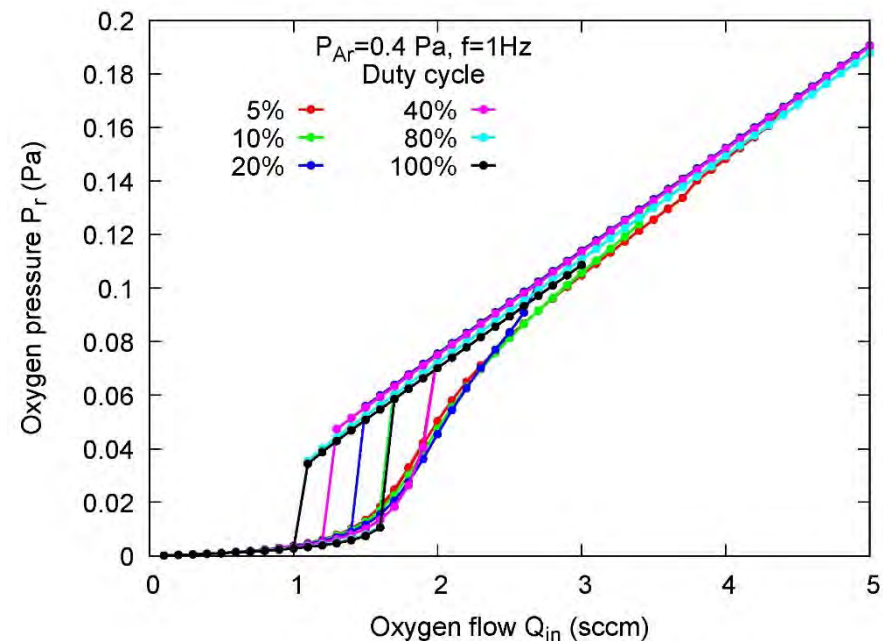
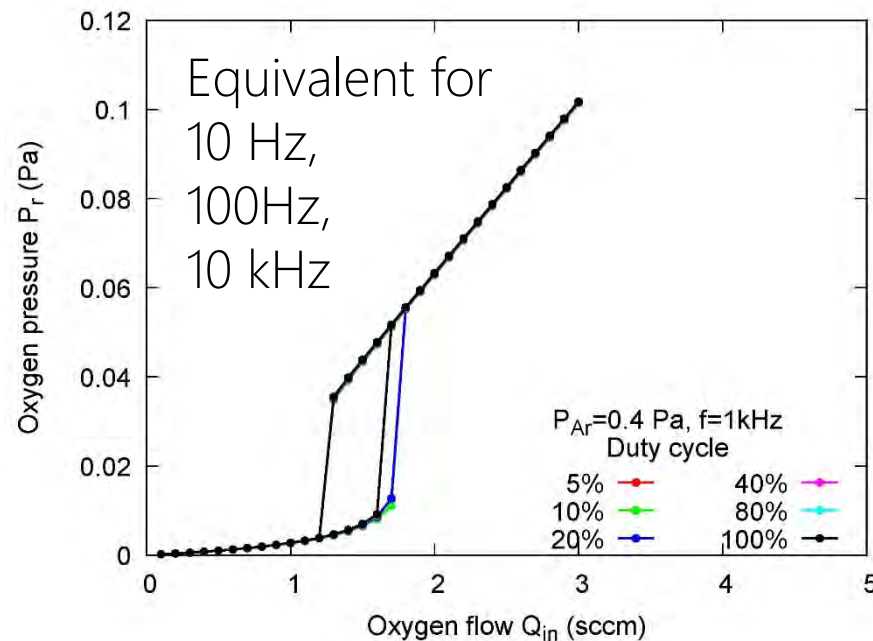


Current pulses



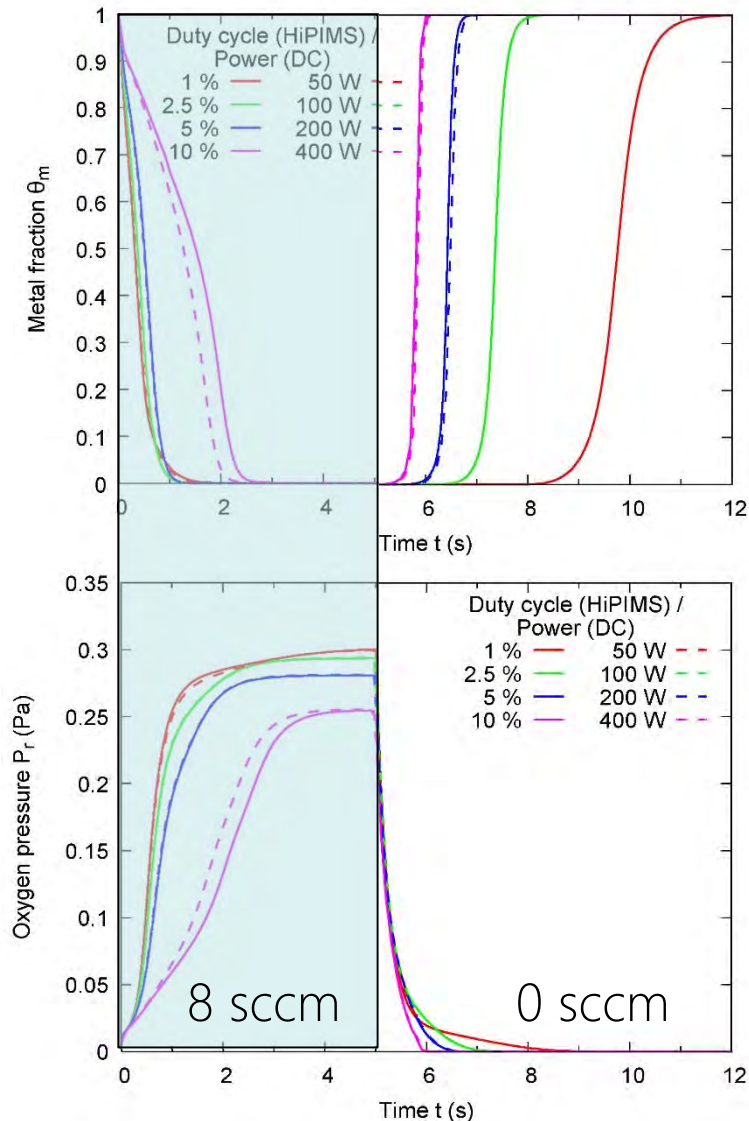
What's the influence of the current pulses?

- ☞ characterized by frequency f , duty cycle d and pulse p ($=d/f$)
- ☞ typical HiPIMS frequencies (100 Hz-10 kHz) and duty cycle (1-10 %)
- ☞ only effect at order 1 Hz
 - ⇒ reactive time dynamics are slower ($\sim 1s$)



constant average power 100 W

Target cleaning



Time dynamics of target poisoning and sputter cleaning for DC and for HiPIMS ($f=1\text{kHz}$)

What's the influence of the average power?

➞ Similar as for the DC regime

- cleaning time scales inversely with power
- poisoning time is only at higher power prolonged

➞ Way of power delivery only starts to matter at high power

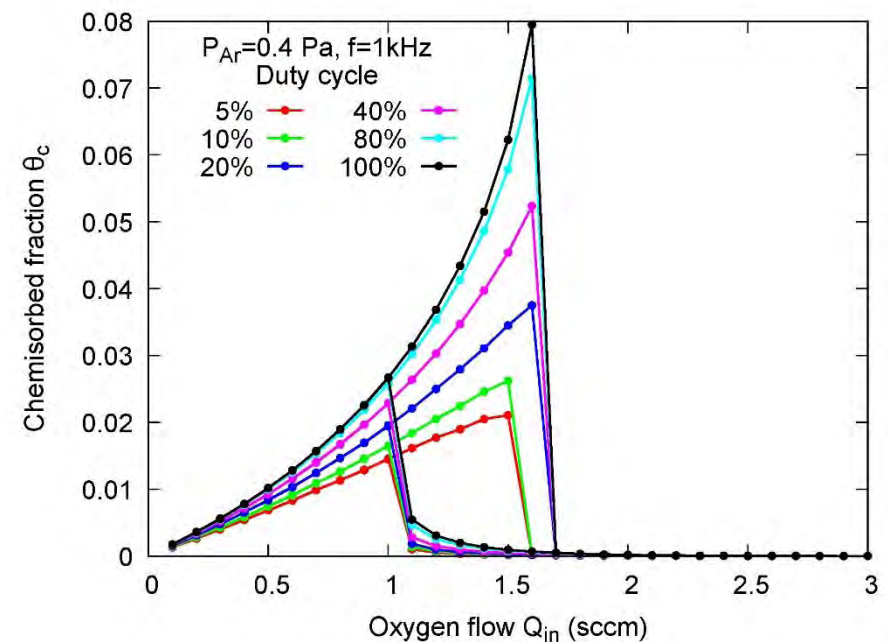
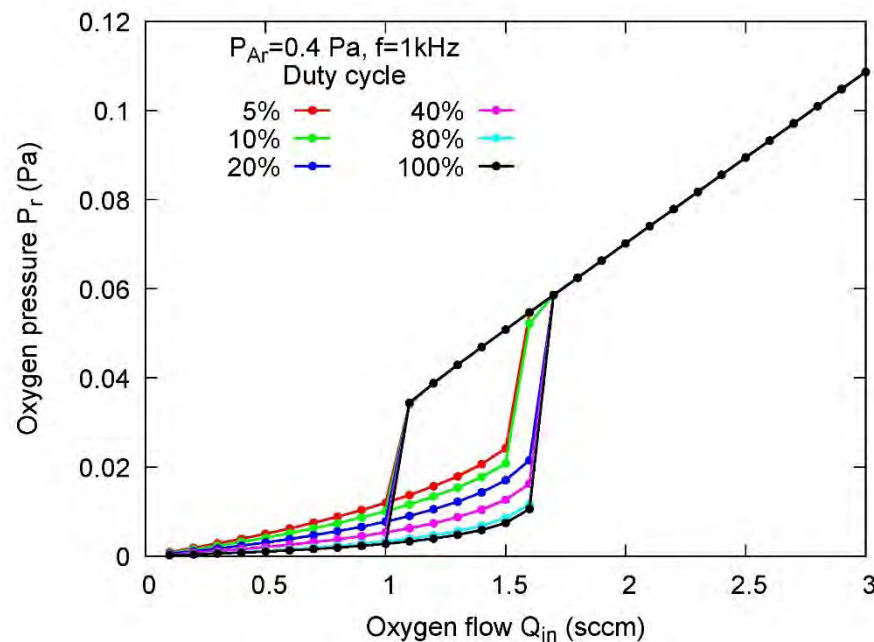
➞ Depoisoning target retarded compared to reactive pressure

Gas reactivity



What's the influence of the gas reactivity?

- ☞ Sticking coefficient target & substrate: 0.1 during pulse-on time
0.01 during pulse-off time
- ☞ Chemisorption is suppressed compared to subsurface oxidation
- ☞ Gas rarefaction would give similar behavior



Returning metal

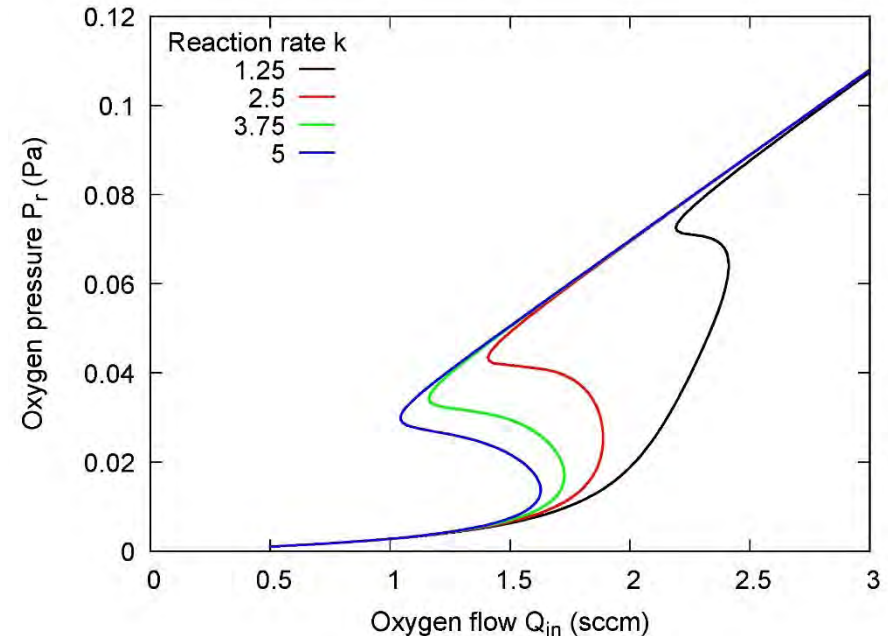
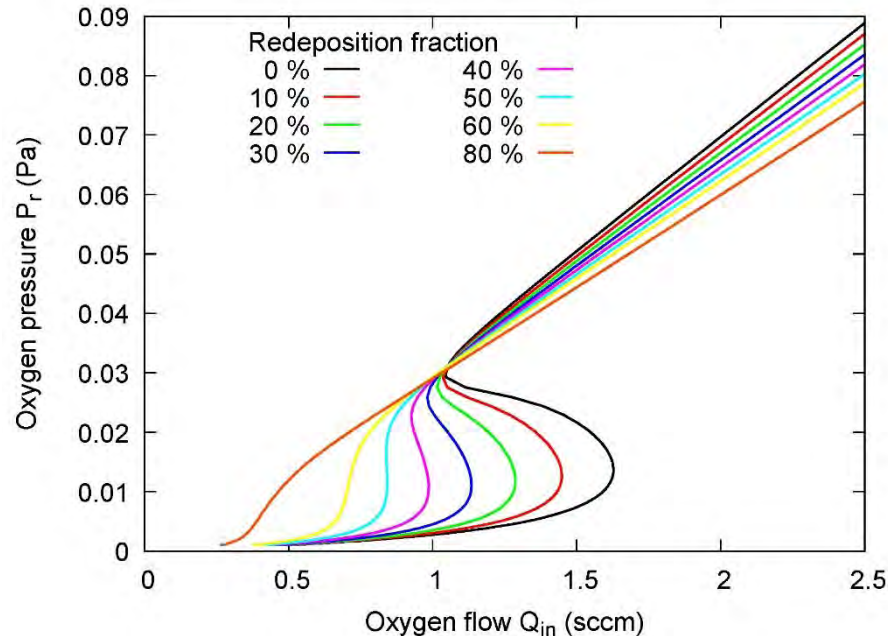


What's the influence of returning metal in DC?

☞ redeposition on the surface of neutral metal eliminates the hysteresis as the 1st critical point shifts faster than the 2nd

but for HiPIMS it are metal ions

☞ metal enrichment in subsurface equivalent with lower oxide production or reaction rate k



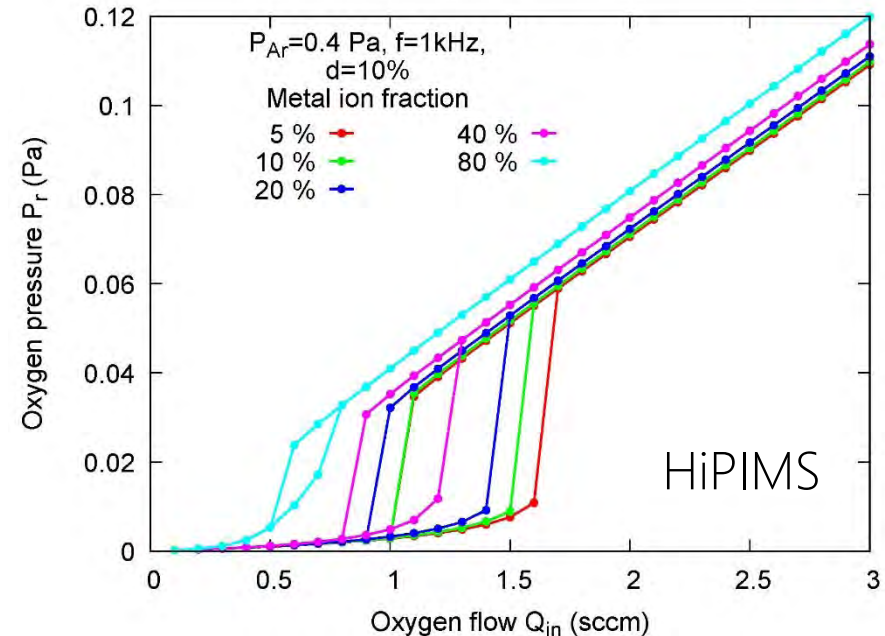
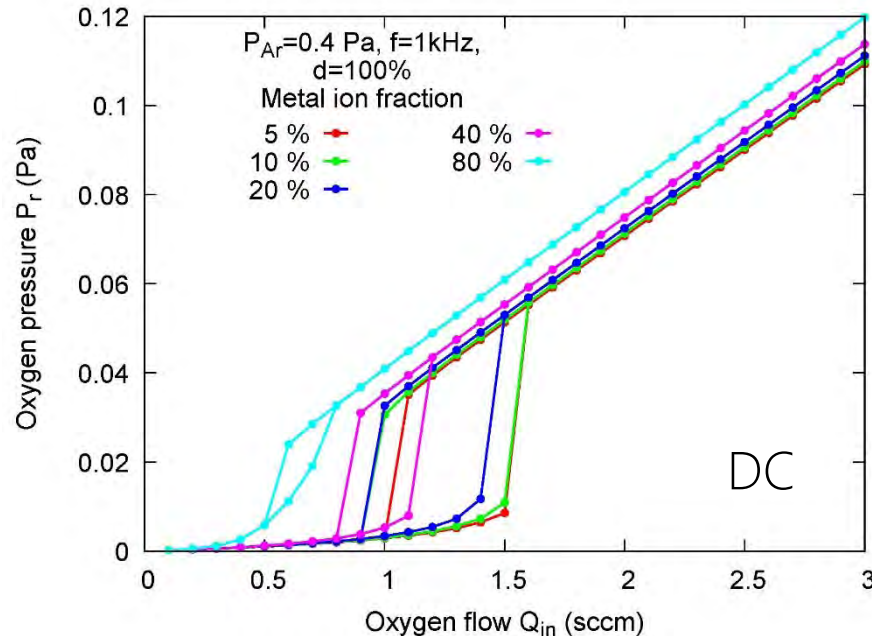
Metal implantation

RSD+PM

What's the influence of the metal implantation?

- ☞ combined effect of "redeposition" and "reaction rate"
- ☞ similar effect for DC and HiPIMS case
- ☞ hysteresis shifts to lower oxygen flows and narrows with increasing fraction of metal ions

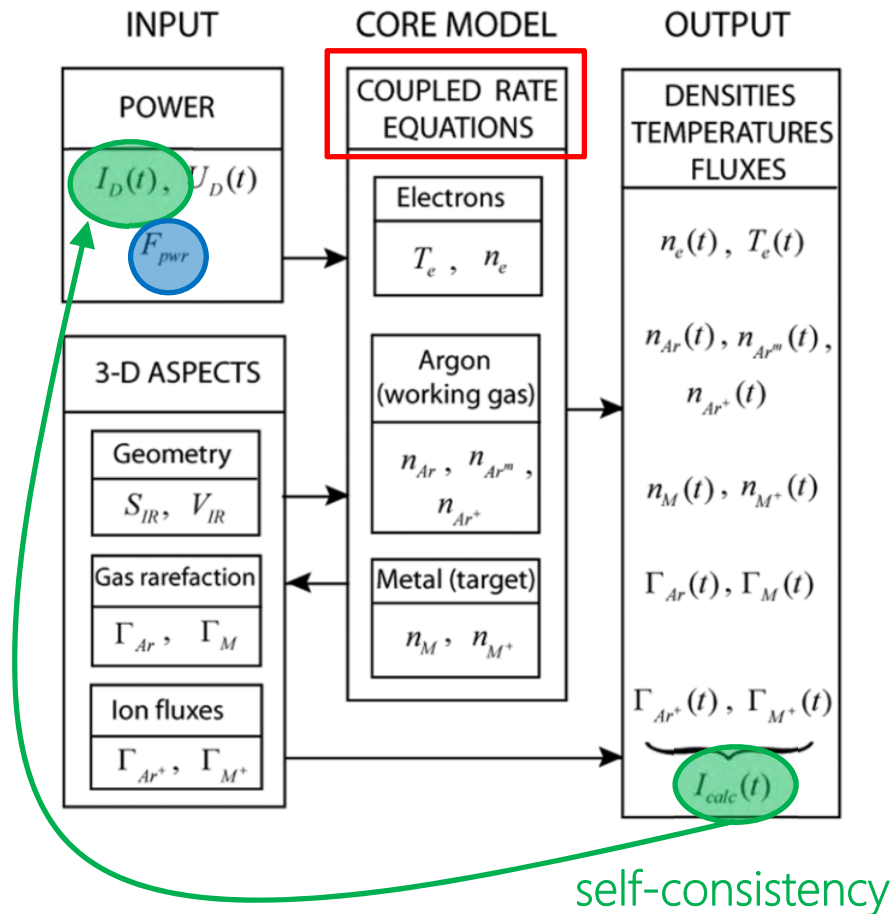
⇒ reduction of hysteresis (but slower than only redeposition)



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IRM for HiPIMS plasma



M.A. Raadu, et al., *Plasma Sources Sci. Technol.* 20 (2011) 065007

IRM

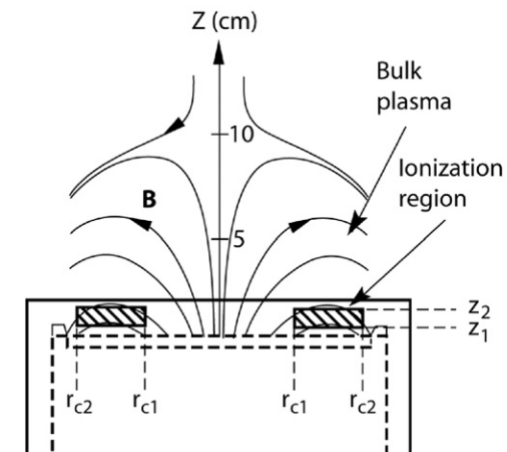
= Ionization Region Model

= global (volume-averaged) model for HiPIMS plasma

... since 2008 by Gudmundsson et al.
and intensively expanded

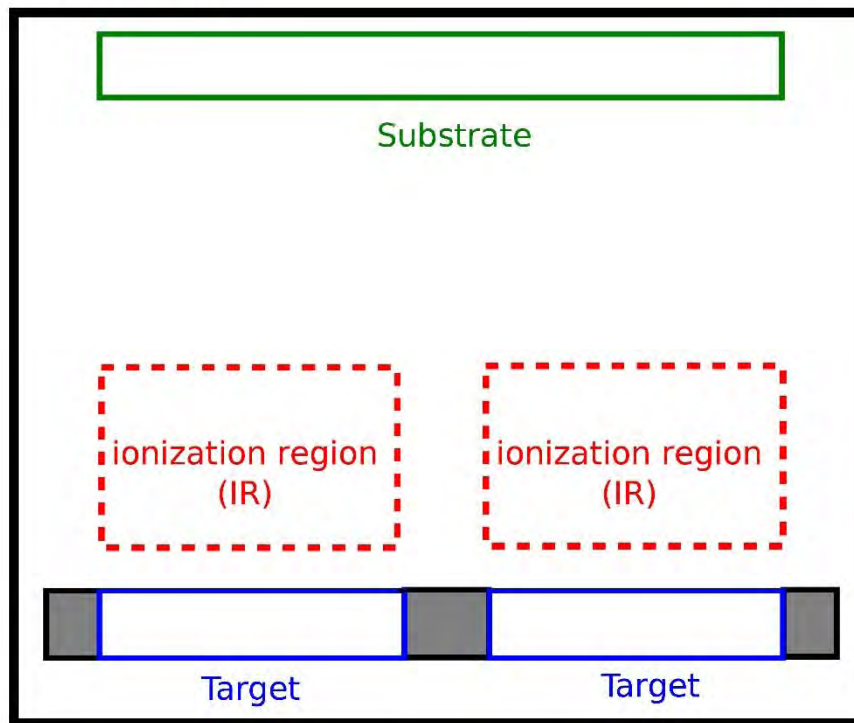
This work "simple version" (Raadu, et al.)

ONE "true" fit parameter F_{pwr}



$$\text{RSD} + \text{IRM} = \text{RSD}^{\text{+IR}}$$

Chamber



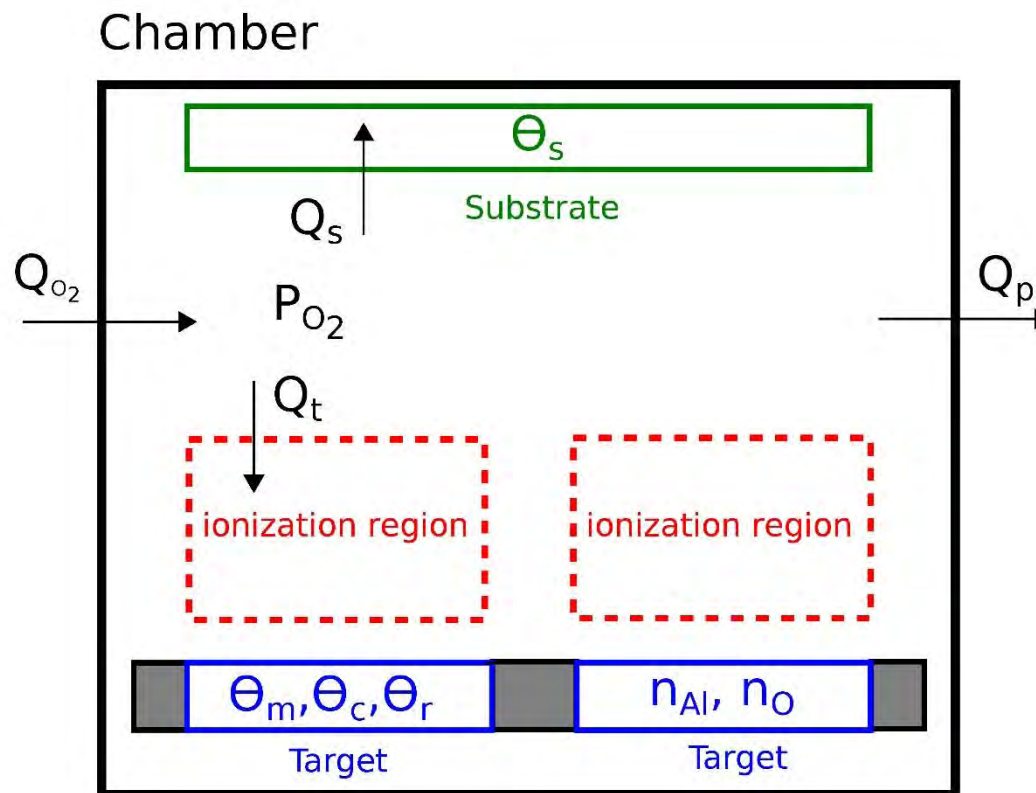
Global model
for
reactive HiPIMS deposition
=
integrate IRM into
modified RSD2013

Four system parts:

1. chamber (0 D)
2. substrate (2 D)
3. target (1D)
4. ionization region (0 D)

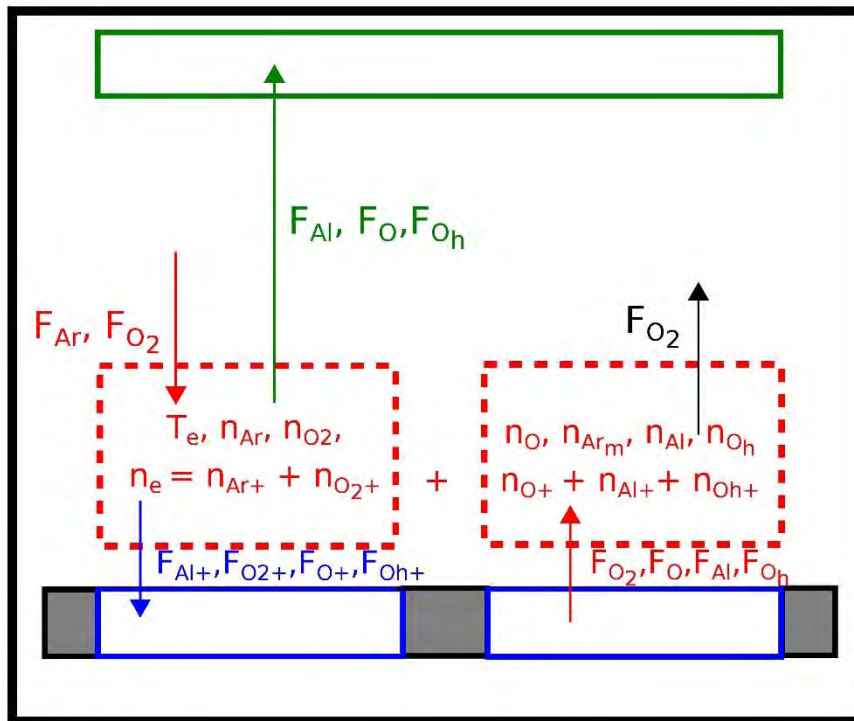


$$\text{RSD} + \text{IRM} = \text{RSD} + \text{IR}$$



RSD variables remain
but
flow q_t into target
becomes
flow q_t into IR

$$\text{RSD} + \text{IRM} = \text{RSD} + \text{IR}$$



IR species

Neutrals:

Ar, Ar_m, O₂, O

Sputtered:

Al, O_h: directed flux

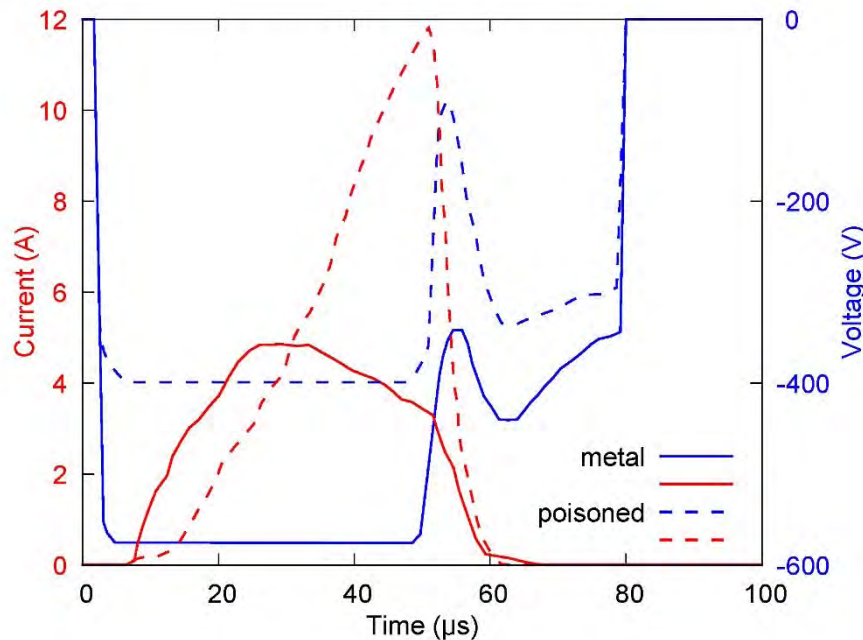
Ions:

single charged

Electron:

T_e power balance
n_e from quasi-neutral
condition

Input for RSD+IR

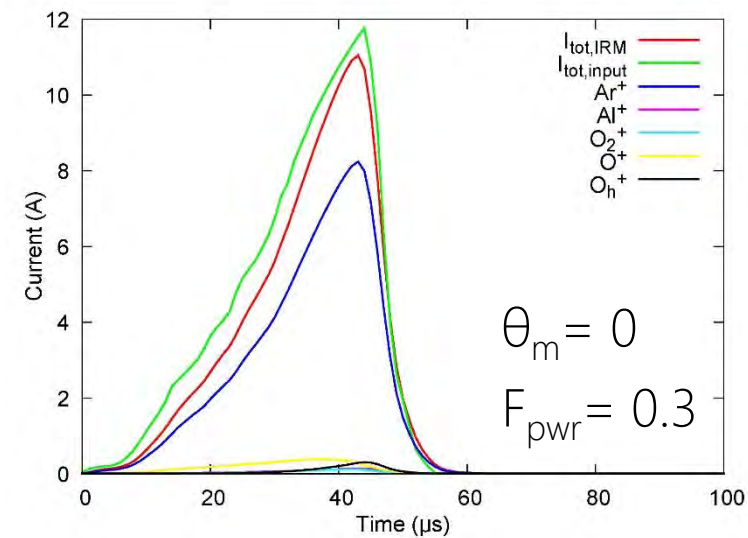
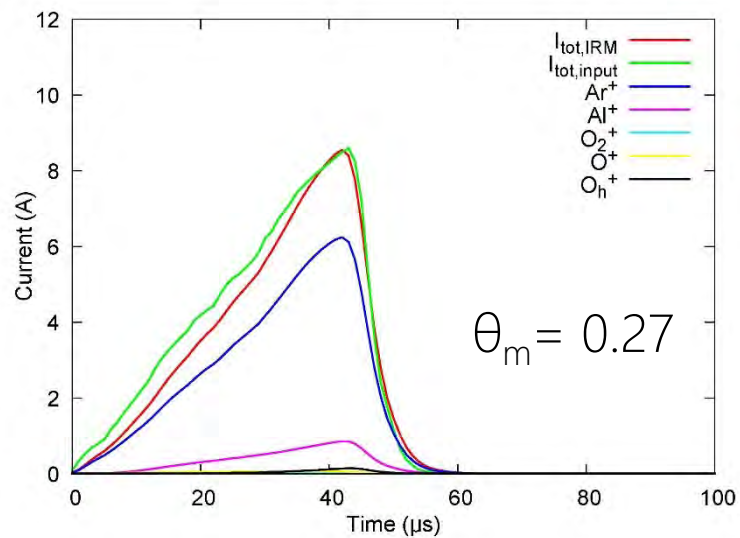
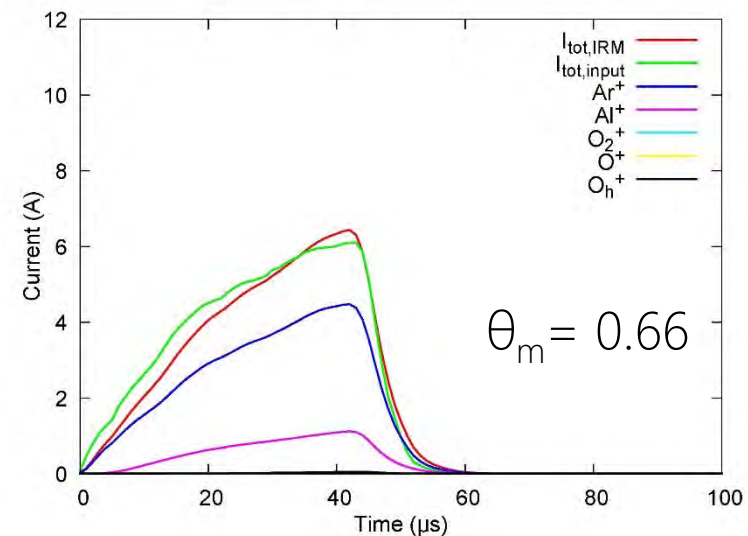
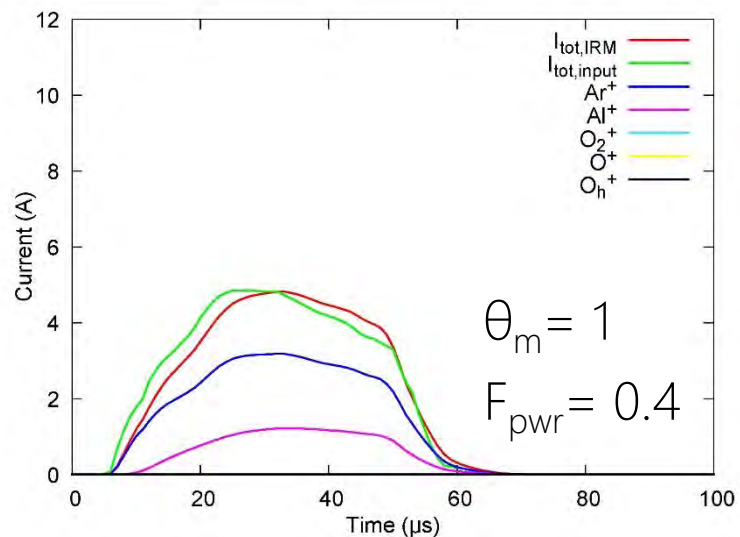


M. Aiempnakit, et al., *J. Appl. Phys.* 113, 133302 (2013)

Input of IVt characteristics

- metal ($\theta_m=1$) and poisoned ($\theta_m=0$) mode
- transition ($0 < \theta_m < 1$) mode
 - ☞ $I = I_m \theta_m + I_r(1-\theta_m)$ & $V = V_m \theta_m + V_r(1-\theta_m)$
 - ☞ $F_{pwr} = F_{pwr, m} \theta_m + F_{pwr, r}(1-\theta_m)$

Locking fitting parameter F_{pwr}

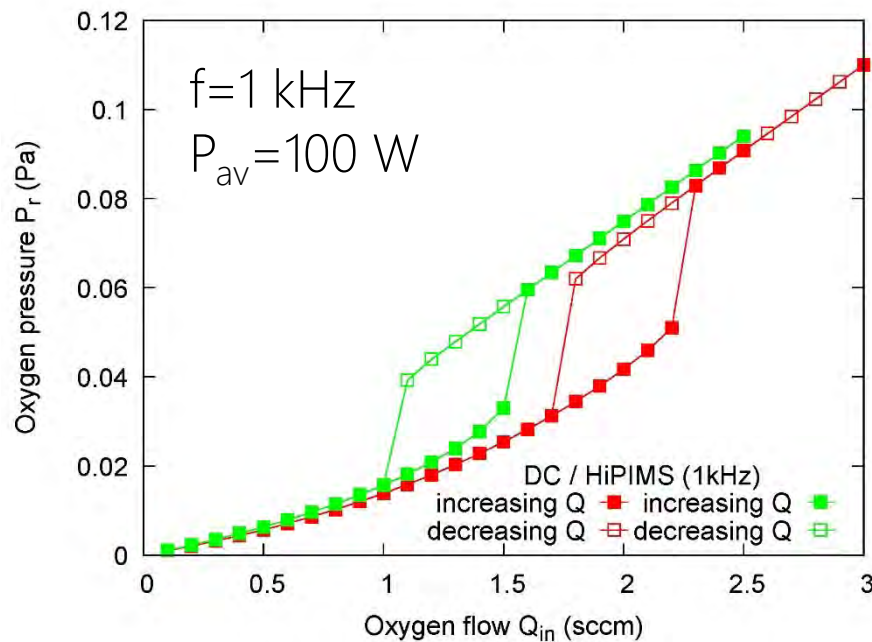


First result



What does this model say?

- ☞ all previous effects are now included
- ☞ hysteresis shifts to lower oxygen flows but does not narrow (yet?)
- ☞ signature of implantation of returning metal



but ...

- ☞ we chose a too simple IRM version
- ☞ ion metal fraction is only ~20 % (HiPIMS) which is expected to double
- ☞ can we transfer our model parameters from DC to HiPIMS?

Outline

- 1 Introduction
- 2 RSD models
- 3 Simulation study
- 4 RSD^{+IR} model
- 5 Conclusion

Future advances

For IR model ...

- potential difference over IR
- two populations electrons "cold" and "warm"
- electron heating = sheath energization + Ohmic heating
- more species (?), more reactions (?)
- speed-up the $\text{RSD}^{+\text{IR}}$ calculation

For a future RSD model ...

- full atomic target description
- recoil/ion mixing
- (ion enhanced) diffusion processes



For experimentalists ...

- a systematic survey

Conclusion

1. Knowledge of reactive DC sputtering can guide us to the unravel the **existence conditions** for a **hysteresis** during reactive HiPIMS.
2. Extensions of the RSD model are used to study the **impact of several effects** claimed to eliminate the hysteresis during reactive HiPIMS.
3. A first coupling between the **RSD2013 model** and the **IR model** is established.
4. Implantation of **ionized sputtered metal** seems to dominate the hysteresis behavior.
5. For a definite answer, **more experimental data** and **modelling** is needed.

Acknowledgements



"Target on growth"

High Performance Computing



DRAFT colleagues:

